Russian Chemical Reviews

Uspekhi Khimii

July 1960

ACYLOXYSILANES

Yu. K. Yur'ev and Z. V. Belyakova

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INTRODUCTION

The term acyloxysilanes in this review denotes monomeric organosilicon compounds in which the silicon atom is joined to at least one acyloxy group. Known types of acyloxysilanes are the tetraacyloxysilanes of general formula $Si(OCOR)_4$, alkylacyloxysilanes $R_xSi(OCOR')_{4-x}$, alkoxyacyloxysilanes $(RO)_xSi(OCOR')_{4-x}$, alkylalkoxyacyloxysilanes $R_x(R'O)_ySi(OCOR'')_{4-x-y}$, and acyloxytrichlorosilanes $Cl_3SiOCOR$. Compounds such as aminoacyloxysilanes, $(NH_2)_xSi(OCOR)_{4-x}$, and (alkylthio)acyloxysilanes, $(RS)_xSi(OCOR')_{4-x}$ are not known.

The first acyloxysilane known was tetraacetoxysilane, prepared by Friedel and Ladenburg[1] in 1868, but up to 1947, i.e. in the 80 years since this class of compound was discovered, no more than 15 papers appeared on the subject, these relating mainly to methods for the preparation of certain acyloxysilanes. Interest in acyloxysilanes in subsequent years has grown considerably, since many have found wide practical application. Thus tetraacyloxysilanes are used in the pharmaceutical industry[2], and their polymeric acylated partial-hydrolysis products are used for the preparation of materials impregnated with silicon dioxide[3].

Alkylacyloxy- and alkylalkoxyacyloxysilanes are widely used to give water-repellent properties to various materials[4-14]. The hydrophobic properties obtained with these reagents are retained for longer periods than those obtained with other organosilicon compounds[15]. Another advantage of acyloxysilanes over, for instance, chlorosilanes arises in their hydrolysis: they do not form corrosive substances such as hydrochloric acid, so that they can be used to impart hydrophobic properties to wool, silk, cotton, leather, wood, paper, iron, magnesium, and other metals[9-12,16-19]. Fabrics impregnated with alkylacyloxysilanes are stable to laundering[9]. Acyloxysilanes, in the wider sense of the term, are also used as plasticisers for lacquers, anti-corrosive and insulating coatings, for the preparation of adhesives, for lubricants and paints withstanding high temperatures, and for the preparation of plastic foams[20-24]. For the analysis of certain volatile organosilicon compounds, the corresponding acetoxy derivatives are prepared[25].

In the last 10–12 years more than 100 papers, theoretical and applied, have been published relating to the synthesis, properties, and uses of acyloxysilanes.

I. METHODS OF PREPARATION OF ACYLOXYSILANES

1. Tetraacyloxysilanes and Acyloxytrichlorosilanes

The simplest, most convenient, and therefore the most used method for the preparation of tetraacyloxysilanes — mixed anhydrides of orthosilicic and organic acids — is the replacement by acyloxy groups of the chlorine of silicon tetrachloride, which is a cheap and readily available industrial material.

In 1868 Friedel and Ladenburg[1] heated a mixture of silicon tetrachloride and a slight excess of acetic acid until no more hydrogen chloride was evolved, and obtained tetraacetoxysilane:

$$SiCl_4 + 4CH_3COOH \longrightarrow Si(OCOCH_3)_4 + 4HCl.$$

Tetrabutyryloxysilane was obtained analogously in 76.6% yield[26]. Later, the method was slightly modified, the reaction being carried out in an inert solvent: in n-heptane, tetraacetoxysilane was obtained in 82% yield and tetrapropionyloxysilane in 80% yield[3], in ether, tetraacetoxysilane in 30% yield[27], and in benzene, tetraformyloxysilane[28] and tetrabenzoyloxysilane in quantitative yield[29]. The tetraacyloxysilanes derived from mono-, di-, and trichloroacetic acids were obtained in benzene in 90–99% yield[30].

The addition of pyridine to the reaction mixture accelerates the reaction and increases the yields of tetraacyloxysilanes[31]. Thus in benzene the tetraacyloxysilanes derived from the following acids were obtained: acetic (96.9% yield), phenylacetic (95.7%), benzoic (97.8%); in n-heptane, n-heptanoic (99.7%), isobutyric (78.2%), isovaleric (88%), and trimethylacetic (86.2%).

Saturated dibasic acids react with silicon tetrachloride in benzene to form acid monoanhydrides of the organic acid with silicic acid, each of the four acid residues attached to the silicon retaining a free carboxyl group[32]:

$$4HOOC[CH_2]_nCOOH + SiCl_4 \longrightarrow Si(OCO[CH_2]_nCOOH]_4 + 4HCl.$$

The hydroxy group of organic hydroxyacids reacts with silicon tetrachloride more easily than the carboxy group, the products being alkoxy- and not acyloxysilanes[33,34]::

$$SiCl_4 + 4HO\,RCOOH \longrightarrow Si(ORCOOH)_4 + 4HCl.$$

However, salicylic acid gives a polymeric reaction product of general formula $[(OC_6H_4COO)_2Si]_n$, indicating that in this case both the hydroxy and carboxy groups react. The reaction of 1 mole of silicon tetrachloride with 4 moles of salicylic acid gave the same reaction product, but in 50% yield[35].

Silicon tetrabromide may be used instead of silicon tetrachloride; tetrabenzoyloxy- and tetrastearoyloxysilanes were prepared in this way[36-38].

The sodium salts of organic acids (with the exception of the formate) react with silicon tetrachloride analogously to the acids themselves, giving the tetraacyloxysilanes[39-41]:

$$4RCOONa + SiCl_4 \longrightarrow Si(OCOR)_4 + 4NaCl.$$

Boiling the mixture of reagents in ether gave, in yields of 58.8–83.8%, the tetraacyloxysilanes derived from propionic, butyric, trichloroacetic, crotonic, stearic, cinnamic, hydrocinnamic, benzoic, *o*-chlorobenzoic, *p*-hydroxybenzoic, and α-naphthoic acids. Tetraacetoxysilane has also been prepared by the reaction of silicon tetrachloride with silver acetate (23%) and lead acetate[27].

A convenient method for the synthesis of tetraacyloxysilanes, particularly crystalline ones, is by the reaction of silicon tetrachloride with an excess of the acid anhydride. The reaction is exothermic; on cooling, the tetraacyloxysilane crystallises, and can be separated by filtration and purified by recrystallisation from the acid anhydride; yields of up to 84.5% are obtained[1,42,43]:

$$4(RCO)_2O + SiCl_4 \longrightarrow Si(OCOR)_4 + 4RCOCl,$$

where R = CH_3 or C_6H_5.

To accelerate the formation of the tetraacetoxysilane, it has been recommended to add thallium acetate, which reacts with the acetyl chloride formed and removes it from the reaction mixture[44]:

$$CH_3COCl + TlOCOCH_3 \longrightarrow TlCl + (CH_3CO)_2O.$$

Tetraacetoxysilane and an alkyl halide are obtained by the reaction of silicon tetrachloride with lower alkyl (up to pentyl) acetates[45]:

$$4CH_3COOR + SiCl_4 \longrightarrow Si(OCOCH_3)_4 + 4RCl.$$

The reaction is different with the acetates of other alcohols and of phenols:

$$4CH_3COOR + SiCl_4 \longrightarrow Si(OR)_4 + 4CH_3COCl$$

where R = iso-C_5H_{11}, C_6H_5, or *p*-$CH_3C_6H_4$;

$$2CH_3COOR + SiCl_4 \longrightarrow 2CH_3COCl + 2RCl + SiO_2,$$

where R = $C_6H_5CH_2$ or $C_6H_5CH_2CH_2$.

However, the literature has indications that completely pure esters not containing traces of moisture do not react with silicon tetrachloride. This has been reported by Ladenburg[46], Rauter[47], and by Yur'ev et al.[48-50], who showed, for example, that silicon tetrachloride reacts with the acid ethyl esters of dibasic acids to form the tetraacyloxysilanes of general formula $Si(OCO[CH_2]_nCOOC_2H_5)_4$.

The synthesis of tetraacyloxysilanes from trichlorosilane and organic acids in an inert organic solvent, e.g n-heptane[3], is of theoretical interest and great practical significance:

$$HSiCl_3 + 4RCOOH \longrightarrow Si(OCOR)_4 + 3HCl + H_2;$$

the acyloxy groups replace the hydrogen atom of the trichlorosilane as well as the chlorine atoms.

The sulphides may also be used for the synthesis of tetraacyloxysilanes[51,52] as well as silicon halides: the tetraacyloxysilanes derived from acetic (25% yield), monochloroacetic (11.5% yield), stearic, and benzoic acids have been prepared by reacting the acids with silicon sulphide:

$$SiS_2 + 4RCOOH \longrightarrow Si(OCOR)_4 + 2H_2S.$$

The tetraacyloxysilanes derived from saturated mono basic acids containing at least six carbon atoms and from aromatic acids such as benzoic and naphthoic can be prepared by a trans-acylation reaction between the acids and tetraacetoxysilane[2,36-38]:

$$Si(OCOCH_3)_4 + 4RCOOH \longrightarrow Si(OCOR)_4 + 4CH_3COOH,$$

$$Si(OCOCH_3)_4 + 2(RCO)_2O \longrightarrow Si(OCOR)_4 + 2(CH_3CO)_2O.$$

The above are the main methods for the synthesis of tetraacyloxysilanes.

The first acyloxytrichlorosilane to be discovered was acetoxytrichlorosilane, first prepared by Goubeau and Mundiel[27] in 20% yield by the action of excess silicon tetrachloride on sodium acetate:

$$SiCl_4 + CH_3COONa \longrightarrow Cl_3SiOCOCH_3 + NaCl.$$

Yur'ev et al.[53-56] showed that acyloxytrichlorosilanes are formed in quantitative yields by the action of excess silicon tetrachloride on monobasic organic acids of the aliphatic, aromatic, and heterocyclic series:

$$RCOOH + SiCl_4 \longrightarrow RCOOSiCl_3 + HCl,$$

where (1) R = CH_3, C_2H_5, n-C_3H_7, iso-C_3H_7, n-C_4H_9, iso-C_4H_9, t-C_4H_9, n-C_5H_{11}, or n-C_7H_{15};

(2) R = C_6H_5, *o*-$CH_3C_6H_4$, *p*-$CH_3C_6H_4$, *o*-ClC_6H_4, *p*-ClC_6H_4, *o*-$NO_2C_6H_4$, *m*-$NO_2C_6H_4$, *p*-$NO_2C_6H_4$, α-$C_{10}H_7$;

(3) R = α-C_4H_3O, α-C_4H_3S.

A necessary condition for the preparation of acyloxytrichlorosilanes is that the reaction be conducted in the liquid phase; the acid must be soluble in silicon tetrachloride or its mixtures with inert solvents such as acetone and ether. Acids which are not soluble in silicon tetrachloride form only tetraacyloxysilanes when heated with it:

$$4\,RCOOH + SiCl_4 \longrightarrow Si(OCOR)_4 + 4\,HCl,$$

where R = p-ClC_6H_4, o-$NO_2C_6H_4$, p-$NO_2C_6H_4$.

Acyloxytrichlorosilanes may also be prepared from excess silicon tetrachloride and the tetraacyloxysilanes, for example, benzoyloxytrichlorosilane in 53.5% yield from tetrabenzoyloxysilane[53]:

$$(C_6H_5COO)_4Si + 3\,SiCl_4 \longrightarrow 4\,C_6H_5COOSiCl_3.$$

Goubeau and Mundiel[27] were unable to obtain acetoxytrichlorosilane from excess silicon tetrachloride and acetic acid or tetraacetoxysilane; in the first case they obtained only tetraacetoxysilane, and made the correct deduction that the acetoxytrichlorosilane formed (I) is unstable and disproportionates to tetraacetoxysilane and silicon tetrachloride (II), hydrogen chloride favouring this reaction:

$$CH_3COOH + SiCl_4 \longrightarrow CH_3COOSiCl_3 + HCl, \quad (I)$$

$$4\,CH_3COOSiCl_3 \rightleftharpoons 3\,SiCl_4 + Si(OCOCH_3)_4. \quad (II)$$

In the second case, in addition to the starting materials, the authors separated acetyl chloride and an organosilicon compound in which the Si : Cl ratio varied in different experiments but was approximately 2 : 3. This compound could not be studied in more detail, because attempts to purify it by distillation caused decomposition to acetyl chloride and acetic anhydride. The following possible conversion reactions were suggested:

$$2\,Cl_3SiCl + 2\,CH_3COOSi(OCOCH_3)_3 \xrightarrow{-CH_3COCl} 2\,Cl_3SiOSi(OCOCH_3)_3 \rightarrow$$

$$\xrightarrow{-(CH_3CO)_2O} Cl_3Si{-}O{-}\underset{\displaystyle COCH_3O}{\overset{\displaystyle COCH_3O}{Si}}{-}O{-}\underset{\displaystyle OCOCH_3}{\overset{\displaystyle OCOCH_3}{Si}}{-}O{-}SiCl_3 \longrightarrow \text{etc.}$$

Two main reactions take place:

$$\equiv Si{-}Cl + CH_3COO{-}Si\equiv \longrightarrow \equiv Si{-}O{-}Si\equiv + CH_3COCl,$$

$$2\equiv Si{-}OCOCH_3 \longrightarrow \equiv Si{-}O{-}Si\equiv + (CH_3CO)_2O.$$

Depending on the excess of silicon tetrachloride, different reaction products are obtained.

The possibility of this type of reaction was also shown by Kapoor et al.[57], who suggested that the formation of acetyl chloride in the reaction of silicon tetrachloride with acetic acid takes place as follows:

$$ClSiCl_3 + 3\,CH_3COOH \longrightarrow ClSi(OCOCH_3)_3 + 3\,HCl,$$

$$SiCl_4 + 4\,CH_3COOH \longrightarrow Si(OCOCH_3)_4 + 4\,HCl,$$

$$ClSi(OCOCH_3)_3 + Si(OCOCH_3)_4 \longrightarrow O\begin{<}\begin{matrix}Si(OCOCH_3)_3\\ \\ Si(OCOCH_3)_3\end{matrix} + CH_3COCl.$$

Hexaacetoxydisiloxane has not been obtained pure, but from analytical data on the silicon and chlorine contents of the product, the authors suggested that they were working with mixtures of hexaacetoxydisiloxane with triacetoxychlorosilane and tetraacetoxysilane.

2. Alkyl- and Arylacyloxysilanes

In this group alkylacyloxysilanes have been described in most detail in the literature, the majority of papers being concerned with alkylacetoxysilanes.

Alkylacyloxysilanes, like the tetraacyloxysilanes, are most often prepared by substituting the acyloxy group for the chlorine in the corresponding alkylhalogenosilanes by reaction with acids or their salts or anhydrides. Thus boiling monobasic organic acids for 40–85 h with excess triethylchlorosilane has given the triethylacyloxysilanes in 26–52% yield[58]:

$$(C_2H_5)_3SiCl + RCOOH \longrightarrow (C_2H_5)_3SiOCOR + HCl,$$

where R = C_3H_7, iso-C_4H_9, or C_6H_{13}.

Dibasic organic acids react with trialkylchlorosilanes under the same conditions as follows[58]:

$$2\,R_3SiCl + HOOC(CH_2)_n COOH \longrightarrow R_3SiOCO(CH_2)_n COOSiR_3 + 2\,HCl,$$

where R = C_2H_5, n = 2, 4, or 7; R = CH_3, n = 4 or 7.

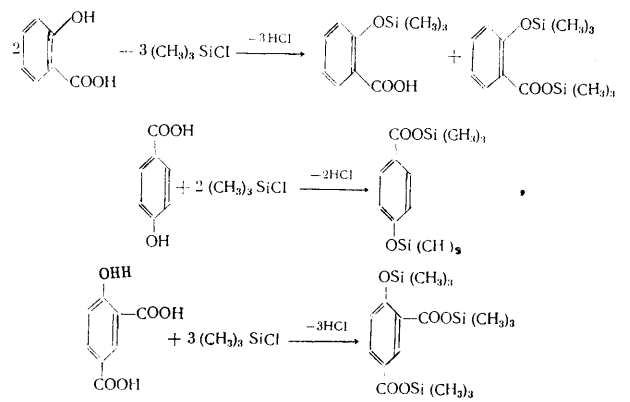
Monobasic amino-acids do not react with trimethylchlorosilane, but dibasic amino-acids and benzoylated monobasic amino-acids react to give the corresponding acyloxysilanes[59]:

$$\begin{matrix}HOOC\\ NH_2\end{>}R{-}COOH + (CH_3)_3SiCl \xrightarrow{-HCl} \begin{matrix}HOOC\\ NH_2\end{>}R{-}COOSi(CH_3)_3,$$

$$C_6H_5CONHCH_2COOH + (CH_3)_3SiCl \xrightarrow{-HCl} C_6H_5CONHCH_2COOSi(CH_3)_3.$$

To accelerate the reaction between alkylhalogenosilanes and organic acids and to increase the yields of alkylacyloxysilanes, it has been recommended to carry out the reaction in benzene in the presence of pyridine[60] or in pyridine (yield 65–76%)[61]; according to the patent literature, the same results are achieved in the presence of salts and anhydrides of the organic acids[4,62,63].

With aromatic hydroxy-acids (salicylic, p-hydroxybenzoic, and 1-hydroxyisophthalic[64]) both the hydroxy and carboxy groups react with trimethylchlorosilane; in pyridine the reaction takes place at room temperature:



The replacement of the halogen by the acyloxy group in alkylhalogenosilanes is much more conveniently carried out by the action of salts of the organic acids (usually the sodium[5,6,65–69], potassium[58,70–72], or silver[73–77] salts),

$$R_xSiHal_{4-x} + (4-x)\,R'COOM \longrightarrow R_xSi(OCOR')_{4-x} + (4-x)\,MHal,$$

by boiling the alkylhalogenosilane with an excess of the salt (sometimes an excess of the silane is used[69]) in the absence

of a solvent or in the presence of inert solvents (benzene[75], toluene[58], ligroin[71], petroleum ether[67,68]). Yields are 40–93%. The reaction is very vigorous with the lower alkylhalogenosilanes. Alkylhalogenosilanes with a long carbon chain (more than eight) react in 10–20 h at 60°–120° in a solvent (ether, toluene)[15]. It is sometimes better to alter the procedure slightly; for example, the yield of dimethyldiacetoxysilane was increased from 50%[65] to 76% when the reaction was effected by circulating dimethyldichlorosilane vapour over sodium acetate[69].

Another interesting reaction is the preparation of diphenyldiacyloxysilanes from diphenyldichlorosilane and alkylacyloxy derivatives of germanium[75]:

$$2C_2H_5Ge(OCOR)_3+3(C_6H_5)_2SiCl_2 \longrightarrow 2C_2H_5GeCl_3\uparrow+3(C_6H_5)_2Si(OCOR)_2.$$

Alkylacyloxysilanes, including those with unsaturated hydrocarbon radicals, may also be prepared by the action of acid anhydrides on alkylhalogenosilanes:

$$R_xSiHal_{4-x}+(4-x)(R'CO)_2O \longrightarrow R_xSi(OCOR')_{4-x}+(4-x)R'COHal.$$

This method has been used almost exclusively for the preparation of alkylacetoxysilanes. The reaction has most often been accomplished by long standing (12–96 h) of the reaction mixture at room temperature[69,72,78–83]; sometimes boiling[7,84,85] or the addition of triethanolamine as catalyst[86–88] is required. Yields are 70–98%. Heating is resorted to only in cases of extreme necessity, since it apparently favours side reactions in which siloxanes are formed. For example, the reaction of dichlorophenyltrichlorosilane with acetic anhydride at room temperature produces dichlorophenyltriacetoxysilane, but at 55° bis(dichlorophenyl)tetraacetoxydisiloxane is obtained[83]:

$$Cl_2C_6H_3SiCl_3 + 3(CH_3CO)_2O \xrightarrow{20^\circ} Cl_2C_6H_3Si(OCOCH_3)_3 + 3CH_3COCl,$$

$$2Cl_2C_6H_3SiCl_3 + 5(CH_3CO)_2O \xrightarrow{55^\circ} [Cl_2C_6H_3Si(OCOCH_3)_2]_2O + 6CH_3COCl.$$

Trialkylacetoxysilanes may also be prepared by acetylating the corresponding trialkylsilanols with acetic acid (up to 80% yield)[89], acetic anhydride[90,91], or acetyl chloride[78,92]:

$$R_3SiOH + CH_3COOH \longrightarrow R_3SiOCOCH_3 + H_2O,$$

where R = C_6H_5

$$R_3SiOH+(CH_3CO)_2O \longrightarrow R_3SiOCOCH_3+CH_3COOH,$$

where R = C_2H_5 or C_6H_5

$$R_3SiOH+CH_3COCl \longrightarrow R_3SiOCOCH_3+HCl,$$

where R = C_6H_5.

If in the reaction with triphenylsilanol the acetyl chloride is used in greater than stoichiometric amounts, triphenylchlorosilane is formed as a result of a side reaction between the triphenylacetoxysilane and acetyl chloride[78]:

$$(C_6H_5)_3SiOCOCH_3 + CH_3COCl \longrightarrow (C_6H_5)_3SiCl + (CH_3CO)_2O.$$

This was confirmed by the preparation of triphenylchlorosilane from triphenylacetoxysilane and acetyl chloride. The reason why attempts to prepare trialkylacyloxysilanes by reaction between the corresponding silanols and acid chlorides were unsuccessful[93] is apparently that excess acid chloride was used. The opinion of Kipping and Lloyd[92] that acetic anhydride does not react with triphenylsilanol, even in the presence of zinc chloride, is thus clearly erroneous.

Sodium derivatives of the silanols also react with acetyl chloride[78]:

$$(C_6H_5)_3SiONa + CH_3COCl \longrightarrow (C_6H_5)_3SiOCOCH_3 + NaCl.$$

Hexaalkyldisiloxanes (but not hexaphenyldisiloxanes) are decomposed by the action of the anhydrides of monobasic organic acids on boiling in the presence of zinc chloride, forming trialkylacyloxysilanes in 90% yield:

$$R_3SiOSiR_3 + (R'CO)_2O \longrightarrow 2R_3SiOCOR'.$$

Under these conditions, the anhydrides of dibasic acids (succinic, maleic) do not react[94]. Trialkylalkoxysilanes react with acetic anhydride in the presence of a catalyst (sulphuric acid[78]) or in its absence[95,96], to produce trialkylacetoxysilanes:

$$R_3SiOR' + (CH_3CO)_2O \longrightarrow R_3SiOCOCH_3 + CH_3COOR'.$$

The reaction of trialkylalkoxysilanes with benzoyl chloride produces trialkylchlorosilanes[96]:

$$R_3SiOR'+C_6H_5COCl \longrightarrow R_3SiCl + C_6H_5COOR'.$$

The replacement of ethoxy groups by acetoxy groups also takes place by the reaction of dimethyldiethoxysilane with diacetoxymethane in the presence of sulphuric acid, the products being dimethyldiacetoxysilane and ethylal[97]:

$$(CH_3)_2Si(OC_2H_5)_2 + (CH_3COO)_2CH_2 \longrightarrow (CH_3)_2Si(OCOCH_3)_2 + (C_2H_5O)_2CH_2.$$

The reaction of trialkylsilanes with organic acids to produce trialkylacyloxysilanes was first proposed and studied in detail by Dolgov et al.[98]:

$$R_3SiH + R'COOH \longrightarrow R_3SiOCOR' + H_2.$$

This reaction is catalysed by sulphuric acid, hydrogen iodide, and iodine, but best of all by a mixture of aluminium and iodine; the rate of reaction increases with increase of the dissociation constant of the acid. Formic acid reacts anomalously with triethylsilane, forming hexaethyldisiloxane, although the reaction is accompanied by the evolution of hydrogen. The following mechanism for the reaction between trialkylsilanes and organic acids was suggested:

$$R_3SiH+I_2 \longrightarrow R_3SiI + HI,$$

$$R_3SiH+HI \xrightarrow{AlI_3} R_3SiI + H_2,$$

$$R_3SiI+HOCOR' \longrightarrow R_3SiOCOR'+HI.$$

The yields of trialkylacyloxysilanes are 81–87%.

Alkylsilanes also form alkylacetoxysilanes by reaction with mercury acetate[98,99] or silver acetate[77]. Triethylsilane and mercury acetate gave triethylacetoxysilane in yields of 72.5–91%:

$$(C_2H_5)_3SiH+Hg(OCOCH_3)_2 \longrightarrow (C_2H_5)_3SiOCOCH_3+Hg+CH_3COOH.$$

Alkylacetoxysilanes are also obtained by the reaction of acetic anhydride with alkylaminosilanes[71]:

$$R_xSi(NHR')_{4-x} + (4-x)(CH_3CO)_2O \longrightarrow R_xSi(OCOCH_3)_{4-x} + (4-x)CH_3CONHR',$$

where R' = hydrogen or alkyl.

Anderson and Fischer[77] found that alkylsilane derivatives such as the sulphides, cyanides, isocyanates, and isothiocyanates react metathetically with silver salts of organic acids, giving the alkylacyloxysilanes:

$$[(C_2H_5)_3Si]_2S + 2AgOCOCH_3 \longrightarrow 2(C_2H_5)_3SiOCOCH_3 + Ag_2S,$$

$$(C_2H_5)_3SiCN + AgOCOCF_3 \longrightarrow (C_2H_5)_3SiOCOCF_3 + AgCN,$$

$$(CH_3)_2Si(CNO)_2 + 2AgOCOCF_3 \longrightarrow (CH_3)_2Si(OCOCF_3)_2 + 2AgCNO,$$

$$(C_2H_5)_2Si(CNS)_2 + 2AgOCOR \longrightarrow (C_2H_5)_2Si(OCOR)_2 + 2AgCNS,$$

where R = CH_3 or CF_3.

For the preparation of alkylacyloxysilanes wherein the acyloxy group is derived from an acid of low volatility, it is sometimes convenient to trans-acylate the alkylacyloxysilanes formed by more volatile acids, by heating with the organic acid while slowly distilling off the more volatile acid[76,77,100]:

$$R_xSi(OCOR')_{4-x} + (4-x)\,R''COOH \longrightarrow R_xSi(OCOR'')_{4-x} + (4-x)\,R'COOH\uparrow.$$

Finally, an interesting reaction from the theoretical point of view is the preparation of triphenylformyloxysilane in 40–55% yields by the thermal rearrangement at 190° of triphenylsilane carboxylic acid[60]:

$$(C_6H_5)_3Si-\underset{\underset{O}{\|}}{C}-OH \xrightarrow{190^\circ} (C_6H_5)_3Si-O-\underset{\underset{O}{\|}}{C}-H.$$

By-products of this reaction are hexaphenyldisiloxane (57% yield), formic acid, and carbon monoxide.

3. Alkylalkoxyacyloxy- and Alkoxyacyloxysilanes

Alkylalkoxyacyloxy- and alkoxyacyloxysilanes are obtained in 14–34% yield by heating alkylalkoxy- and alkoxysilanes respectively with acid anhydrides[101,102]:

$$R_xSi(OR')_{4-x} + y\,(R''CO)_2O \longrightarrow R_xSi(OR')_{4-x-y}(OCOR'')_y + y\,R''COOR',$$

where x = 0, 1, or 2, and y = 1, 2, or 3.

The low yields are due to the dissociation of the reaction products in the anhydride medium, so that a side reaction leading to the formation of polyorganosiloxanes takes place[101], e.g.:

$$C_2H_5Si(OR)_2(OCOCH_3) \xrightarrow{(CH_3CO)_2O} C_2H_5Si(OR)_2O^- + CH_3CO^+,$$

$$C_2H_5Si(OR)_2(OCOCH_3) \xrightarrow{(CH_3CO)_2O} C_2H_5Si(OR)(OCOCH_3)^+ + (OR)^-,$$

$$C_2H_5Si(OR)(OCOCH_3)^+ + C_2H_5Si(OR)_2O^- \longrightarrow (C_2H_5)(RO)(CH_3COO)Si-O-Si(OR)_2C_2H_5.$$

The formation of polysiloxanes may become the main reaction in the reaction of alkylalkoxysilanes or alkoxysilanes with phthalic anhydride[103].

When a trialkoxysilane reacts with acetic anhydride[104], one alkoxy group is first replaced by the acyloxy group to form a dialkoxyacyloxysilane; with further heating and with excess acetic anhydride, the reaction proceeds further, with substitution of the hydrogen atom to produce a dialkoxydiacyloxysilane:

$$(RO)_3SiH + (CH_3CO)_2O \rightarrow (RO)_2SiH(OCOCH_3) + CH_3COOR,$$

$$(RO)_2SiH(OCOCH_3) + (CH_3CO)_2O \rightarrow (RO)_2Si(OCOCH_3)_2 + CH_3CHO.$$

The literature contains contradictory reports on the action of organic acids on alkoxysilanes. According to some[105,106], alkoxyacyloxysilanes and the corresponding alcohols are formed:

$$Si(OR)_4 + R'COOH \rightarrow (RO)_3SiOCOR' + ROH,$$

while others[20,107] assert that the reaction produces esters and silicic acid:

$$Si(OR)_4 + 4R'COOH \rightarrow 4R'COOR + Si(OH)_4.$$

These differences are apparently due to the different reaction conditions.

Alkoxyacyloxysilanes can also be obtained by the action of organic acids on alkoxyaminosilanes[108]:

$$(RO)_2Si(NH_2)_2 + 4R'COOH \rightarrow (RO)_2Si(OCOR')_2 + 2R'COONH_4.$$

The specific method of substituting the alkoxy group for the acyloxy group in acyloxysilanes containing at least two acyloxy groups can also be used for the synthesis of alkoxyacyloxy- and alkylalkoxyacyloxysilanes. The reaction of acyloxysilanes with primary and secondary alcohols is exothermic; the acid liberated in the reaction should be distilled off at as low a temperature as possible[69,70,81,109,110]. Tertiary alcohols react only by heating to 100°–140°[69,110]:

$$R_xSi(OCOR')_{4-x} + yR''OH \rightarrow R_xSi(OCOR')_{4-x-y}(OR'')_y + yR'COOH.$$

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All these methods for the synthesis of acyloxysilanes (with the exception of the last) involve the replacement by an acyloxy group of various atoms or radicals joined to the silicon atom. They may be represented schematically as follows:

(1) $\equiv Si-Hal \xrightarrow{+RCOOH,\ RCOOM,\ (RCO)_2O} \equiv Si-OCOR$,

(2) $\equiv Si-H \xrightarrow{+RCOOH,\ RCOOM,\ (RCO)_2O} \equiv Si-OCOR$,

(3) $\equiv Si-OH \xrightarrow{+RCOOH,\ (RCO)_2O,\ RCOCl} \equiv Si-OCOR$,

(4) $\equiv Si-O-Si \equiv \xrightarrow{+(RCO)_2O} 2 \equiv Si-OCOR$,

(5) $\equiv Si-OR' \xrightarrow{+(RCO)_2O} \equiv Si-OCOR$,

(6) $\equiv Si-N \langle \xrightarrow{+RCOOH,\ (RCO)_2O} \equiv Si-OCOR$,

(7) $\equiv Si-S- \xrightarrow{+RCOOH,\ RCOOM,\ (RCO)_2O} \equiv Si-OCOR$,

(8) $\equiv Si-CN \xrightarrow{+RCOOM} \equiv Si-OCOR$,

(9) $\equiv Si-CNO \xrightarrow{+RCOOM} \equiv Si-OCOR$,

(10) $\equiv Si-CNS \xrightarrow{+RCOOM} \equiv Si-OCOR$,

(11) $\equiv Si-COOH \xrightarrow{\text{heat to } 190^\circ} \equiv Si-OCOH$,

(12) $\equiv Si-OCOR' \xrightarrow{RCOOH,\ (RCO)_2O} \equiv Si-OCOR$,

(13) $\equiv Si(OCOR)_2 \xrightarrow{R'OH} \equiv Si(OCOR)(OR')$.

The best methods for the synthesis of tetraacyloxy- and alkylacyloxysilanes are those based on the reaction of halogenosilanes with acids or their salts and anhydrides, but such methods cannot be used to prepare alkoxyacyloxy- or alkylalkoxyacyloxysilanes; these are most often prepared by methods such as the reaction of acid anhydrides with alkoxysilanes or of alcohols with acyloxysilanes.

The intermediate formation of (alkylthio)acyloxysilanes (which have not as yet been separated as individual compounds) is assumed in the reaction between tri(alkylthio)silanes and acetic anhydride to form thioesters (I):

$$HSi(SR)_3 + (CH_3CO)_2O \longrightarrow CH_3COSR + [CH_3COOSiH(SR)_2], \quad (I)$$

$$[CH_3COOSiH(SR)_2] \longrightarrow CH_3COSR + \left(-O-\underset{\underset{SR}{|}}{\overset{\overset{H}{|}}{Si}}-\right)_x. \quad (II)$$

Wolinski et al.[111] assume the formation of the unstable second reaction product di(alkylthio)acetoxysilane (I), which then decomposes according to Eqn. (II) to give a thioester and an organosilicon polymer.

II. REACTIONS OF ACYLOXYSILANES

1. Reactions of Tetraacyloxysilanes

Tetraacyloxysilanes are liquid (propionyloxy[39] and butyryloxy[41]), amorphous (formyloxy[28]), or crystalline (acetoxy[1,42], benzoyloxy[40,51], trichloracetoxy, stearoyloxy, naphthoyloxy, and others[41]). They are soluble in inert organic solvents such as benzene, acetone, and ether, and are very hygroscopic. On heating they decompose to acid anhydride and silica:

$$Si(OCOR)_4 \longrightarrow 2(RCO)_2O + SiO_2.$$

Tetraacetoxysilane decomposes at 160°–170°[1], but in a vacuum (5–6 mm Hg) it sublimes without noticeable decomposition at 148°. Tetrakis(monochloroacetoxy)silane decomposes even at 50°–60° (6 mm Hg), while tetraformyloxysilane cannot be obtained pure, since it always contains silica. This decomposition reaction is the basis for the preparation of the anhydrides of acetic[112] (yields 75–96%), propionic[113], and butyric (yield 76.6%[26]) acids.

Tetraacyloxysilanes derived from saturated monobasic acids are hydrolysed instantaneously; tetrabenzoyloxysilane reacts with water somewhat more slowly[40]. According to Khaskin[114,115] the hydrolysis of tetraacetoxysilane by the action of water containing labelled oxygen takes place predominantly by the following reaction, indicating the stability of the $\geqslant Si-O$ bond:

$$\geqslant SiO-COCH_3 + H\dot{O}-H \longrightarrow \geqslant SiO-H + CH_3CO-\dot{O}H.$$

Tetraacyloxysilanes react vigorously with alcohols; two different reaction schemes have been proposed. According to Friedel and Ladenburg's results[1], esters and silicic acid are formed (III), while Malatesta[51] considers that the products are organic acids and tetraalkoxysilanes (IV):

$$Si(OCOR)_4 + 4R'OH \longrightarrow 4RCOOR' + Si(OH)_4, \quad (III)$$

$$Si(OCOR)_4 + 4R'OH \longrightarrow Si(OR')_4 + 4RCOOH. \quad (IV)$$

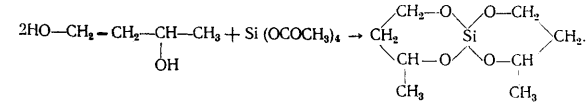
It has been found recently[110] that even in the cold, tetraacetoxysilane reacts exothermically with primary and secondary alcohols, forming (depending on the ratios of reactants) tetraalkoxysilanes or alkoxyacetoxysilanes:

$$Si(OCOCH_3)_4 + xROH \rightleftarrows (CH_3COO)_{4-x}Si(OR)_x + xCH_3COOH \quad (V)$$

where $x = 1-4$.

These products are obtained smoothly only when the reactants are used in molar proportions and the resulting acetic acid is removed by distillation in a vacuum. If the acetic acid is distilled at normal pressure or the reaction mixture is first heated, the yield of alkoxy derivatives falls sharply, and the alkyl acetate and a gel of silicon polymer are obtained. These experimental results were explained as follows: above 80°–90° reaction (V) may become reversible, and the acetoxysilane acetylates the alcohol, forming the acetate; the ester is formed by esterification of the alcohol with acetic acid, the $(CH_3COO)_{4-x}Si(OR)_x$ acting as water-removing agent. It must be added that tertiary alcohols react with much more difficulty than primary and secondary, reaction only taking place on heating to 100°–140°; for example, not more than three acetoxy groups can be replaced by t-butoxy groups.

The reaction of tetraacetoxysilane with 1,3-butandiol produces in good yield the spirocyclic orthosilicic acid ester 4,8-dimethyl-1,5,7,11-tetraoxa-6-silaspiro[5,5]undecane[116]:



Contrary to this reaction, 1,4-butandiol and 1,5-pentandiol gave only the acetates[116]:

$$2HO-[CH_2]_n-OH + Si(OCOCH_3)_4 \rightarrow 2CH_3COO-[CH_2]_n-OCOCH_3 + Si(OH)_4 \quad (n = 4-5).$$

Tetraacetoxysilane reacts with dry ammonia to form acetamide and silicic acid[1,117]:

$$Si(OCOCH_3)_4 + 4NH_3 \rightarrow 4CH_3CONH_2 + Si(OH)_4.$$

Yur'ev, Belyakova, and coworkers showed that the acylation of ethyl-, diethyl-, and dibutylamine with tetraacyloxysilanes derived from saturated monobasic organic acids is a convenient method for the preparation of *N*-alkyl and *N*,*N*-dialkyl acid amides (yields 60–90%)[54,117,118]:

$$4R'R''NH + Si(OCOR)_4 \rightarrow 4RCONR'R'' + Si(OH)_4;$$

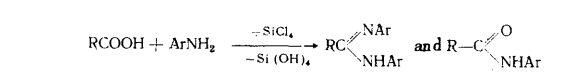
(1) R′=H; R″=C_2H_5; R=CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, iso-C_4H_9, n-C_5H_{11};

(2) R′=R″=C_2H_5; R=CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, iso-C_4H_9, n-C_5H_{11};

(3) R′=R″=C_4H_9; R=CH_3, C_2H_5, n-C_3H_7, n-C_5H_{11}.

N,*N*-diethylamides of aromatic acids (benzoic, *o*- and *p*-toluic) are obtained in lower yields (24–63%). The reduced acylating power of aromatic tetraacyloxysilanes is due to the greater strength of these acids[117]. The reaction of tetraacetoxy- and tetrabenzoyloxysilanes with aniline and methylaniline has given the corresponding anilides[51,118]; however, in the reaction of the monochloroacetoxysilane with aniline, only the molecular compound of composition $ClCH_2COOH \cdot C_6H_5NH_2$ has been separated[51].

The arylamides of various monobasic acids (including hydroxy- and amino-acids) have been obtained by reacting the corresponding acids with silicon tetrachloride and the arylamine. Acyloxysilanes are apparently intermediates in this reaction; in the case of 2,3-hydroxynaphthoic acid a yellow polymeric substance of composition $[(OCOC_{10}H_6O)_2Si]_x$ was separated. If the reaction is carried out in excess silicon tetrachloride, diarylamidines are obtained in 50–79% yield, often together with the arylamides[119,120]:



Acylation of phenyl- and acetylhydrazine with the tetraacyloxysilanes derived from monobasic organic acids gives the corresponding acid phenyl- and acetylhydrazides (yields 61–85%)[54,117]:

$$4R'NHNH_2 + Si(OCOR)_4 \rightarrow 4R'NHNHCOR + Si(OH)_4$$

where R′ = C_6H_5 or CH_3CO.

Yur'ev and Belyakova obtained only the mono-*N*,*N*-diethylamide of succinic acid in the acylation of diethylamine with tetrasuccinyloxysilane, thus convincingly confirming the structural formula suggested for the acyloxysilanes derived from dibasic acids, in which each of the four acid

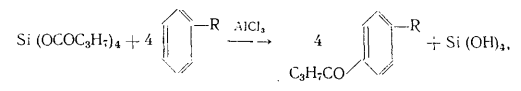
residues contains a free carboxyl group[32]:

$$(HOOC[CH_2]_3COO)_4Si + 4NH(C_2H_5)_2 \xrightarrow{-Si(OH)_4} 4HOOC(CH_2)_2CON(C_2H_5)_2.$$

Like the anhydrides of organic acids, the tetraacyloxysilanes can acylate phenols, and can acylate the benzene nucleus in the Friedel–Crafts reaction. Thus in 1947 Petrov and Itkina[121] used tetrabutyryloxysilane as the acylating agent for the preparation of phenyl butyrate:

$$Si(OCOC_3H_7)_4 + 4C_6H_5OH \xrightarrow{70°} 4C_3H_7COOC_6H_5 + Si(OH)_4.$$

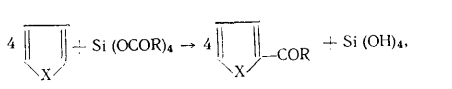
These workers were the first to condense tetrabutyryloxysilane with benzene and toluene in the presence of aluminium chloride to obtain propyl phenyl ketone (in low yield) and propyl-*p*-tolyl ketone (37% yield) respectively:



where R = H or CH_3.

Somewhat later, Petrov and Lagucheva[29] carried out analogous condensations of other tetraacyloxysilanes with benzene, toluene, and chlorobenzene, and obtained the following ketones: benzophenone (58% yield), a mixture of phenyl *o*-tolyl and phenyl *p*-tolyl ketones (86%), methyl *p*-tolyl ketone (62.7%), methyl *p*-chlorophenyl ketone (45.4%), and acetophenone (47%). Tetraformyloxysilane has also been used to acylate phenol and toluene[28]; the yield of phenyl formate reached 46%, but the yield of *p*-tolualdehyde was very low, the reaction product consisting mainly of crystalline substances which are further conversion products of the *p*-tolualdehyde. According to Petrov and Lagucheva's results[29], the pure tetraacyloxysilane, separated from the solvent in which it was prepared, had a lower acylating power than the same acyloxysilane when used in solution in the solvent without separation; however, it was later shown by other workers that this is incorrect.

Yur'ev, Elyakov, and coworkers in 1952 studied the acylation with tetraacyloxysilanes of the five-membered heterocyclic compounds furan and thiophene[122–124] and selenophene[125,126]. In the presence of anhydrous stannic chloride in benzene, there were obtained methyl-2-furyl ketone (7% yield), and ketones of the thiophene (53–96% yields) and selenophene (62–82% yields) series:



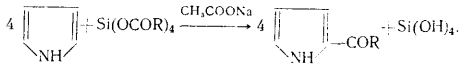
where X = O, R = CH_3;

X = S, R = CH_3, C_2H_5, n-C_3H_7, iso-C_3H_7, n-C_4H_9, s-C_4H_9, t-C_4H_9, n-C_5H_{11}, n-C_7H_{15}, n-$C_{15}H_{31}$, n-$C_{17}H_{35}$, C_5H_9, C_6H_{11}, C_6H_5, or $C_{10}H_{11}$;

X = Se, R = C_2H_5, s-C_4H_9, n-C_4H_9, C_5H_9, C_6H_5.

The yields of 2-thienyl ketones decrease as branching of the carbon chain increases. A peculiarity of acylation with tetraacyloxysilanes is the need to employ equimolar or even greater quantities of catalyst (as in acylation with acid chlorides), whereas with acid anhydrides catalytically small quantities are used. A detailed study of the acetylation of thiophene and benzene with tetraacetoxysilane in the presence of various condensation agents[127] has shown that in the acetylation of thiophene in the presence of titanium tetrachloride, with a molar ratio of catalyst to acetic acid of 0.4 : 1, the yield of acetylthienone at 60° was 37%, and with a ratio of 0.83 : 1 reached 93.5%*; tetraacetoxysilane, which acetylates thiophene in the presence of anhydrous $BeCl_2$, $ZnCl_2$, $BF_3 \cdot (C_2H_5)_2O$, and $TiCl_4$, does not acetylate benzene under the same conditions; the acetylating agent is the acetoxysilane itself; in activity in the acylation of the aromatic nucleus, tetraacyloxysilanes occupy the last place in the series acid chloride > acid anhydride > tetraacyloxysilane; the acylation of thiophene with tetraacetoxysilane prepared in benzene and not isolated from it, and with pure tetraacetoxysilane, give identical results under identical conditions in benzene in the presence of stannic chloride as catalyst.

Yur'ev and Elyakov acylated the pyrrole nucleus by heating pyrrole with a tetraacyloxysilane derived from a saturated monobasic acid (after removal of the solvent in a vacuum) at 180° in the presence of anhydrous sodium acetate; ketones of the pyrrole series were obtained in yields of 34–56%[128]:

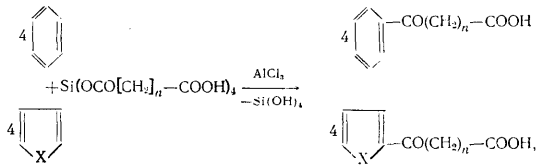


In the acylation of indole in the presence of stannic chloride, the yield of 3-acetylindole did not exceed 21%, with respect to reacted indole[128].

Unsaturated monobasic organic acids (vinylacetic, allylacetic, Δ^3-cyclohexenecarboxylic) also react with silicon tetrachloride to form the corresponding tetraacyloxysilanes, which on condensation with benzene (in the presence of aluminium chloride), thiophene, and selenophene (in the presence of stannic chloride) give the corresponding unsaturated ketones, although in low yields (20–30%) because of much resinification. When acylating benzene, the reaction is also complicated by alkylation of the benzene by the resulting unsaturated ketone[129].

The tetraacyloxysilanes derived from saturated dibasic organic acids are prepared by reacting silicon tetrachloride with the acids in benzene, and, as indicated above, have a free carboxyl group on each of the four acid residues attached to the silicon atom; therefore, as Yur'ev, Elyakov, and Belyakova showed, they acylate benzene in the presence of aluminium chloride to form ω-benzoylalkanoic acids (yields 51–96%)[48]; in the acylation of thiophene in nitrobenzene in the presence of aluminium chloride, ω-(2-thenoyl)alkanoic acids are obtained in 33–77% yields. In neither case were diketones detected. These tetraacyloxysilanes do not acylate thiophene in benzene in the presence of stannic chloride[130].

Selenophene was acylated with tetrasuccinyloxysilane at -30° in a mixture of nitrobenzene and carbon disulphide in the presence of aluminium chloride, but the yield of β-2-selenoyl)propionic acid was only 7%[49]:



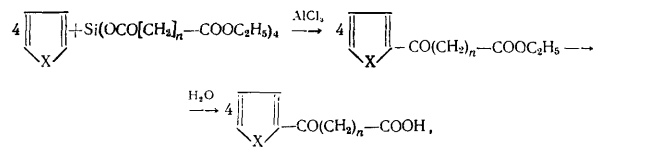
where X = S or Se.

* The quantity of catalyst and yield of ketones were calculated with respect to the acid used in the preparation of the tetraacyloxysilane.

The same workers showed that the tetraacyloxysilanes derived from the ethyl half-esters of dibasic acids acylate benzene (in the presence of aluminium chloride) and thiophene and selenophene (in the presence of stannic chloride). For example, the acylation of benzene with the acyloxysilane derived from monoethyl malonate gave ethyl benzoylacetate in 33% yield[48]:

$$4C_6H_6+Si(OCOCH_2COOC_2H_5)_4 \longrightarrow 4C_6H_5COCH_2COOC_2H_5+Si(OH)_4 .$$

The acylation of thiophene and selenophene with the acyloxysilanes derived from the monoethyl esters of dibasic acids, with subsequent hydrolysis of the resulting keto-acid esters, gave δ-(2-thenoyl)valeric acid (66% yield) and ω-(2-selenoyl)-alkanoic acids (20–42% yields)[49]:



where X = S or Se.

Yur'ev, Belyakova, and Volkov showed that the tetraacyloxysilanes derived from α-halogeno saturated organic acids have lower acylating activity than the corresponding unsubstituted compounds, and can only be used in acylation reactions in the presence of strong condensation agents such as aluminium chloride. On the basis of the acylation of benzene with the compounds derived from acetic, monochloro-, dichloro-, and trichloroacetic acids, it was shown that the greater the strength of the acid, the lower the acylating activity of its derivative. The acylation of benzene with tetra(β-bromopropionyloxy)silane produces, depending on the conditions, either β-bromopropiophenone (70% yield) or a mixture of β-hydroxy- and β-phenylpropiophenone[30]. Tetra(β-chloropropionyloxy)silane and tetra(γ-chlorobutyryloxy)silane only exhibit strong alkylating properties[131].

The acylation of benzene and, particularly, five-membered heterocyclic rings, with tetraacyloxysilanes has a number of advantages over methods of acylation using acid chlorides or anhydrides; the tetraacyloxysilanes can be used in the solvent in which they are prepared, and so are more readily available than the acid chlorides and anhydrides, particularly those with branched chains or of high molecular weight. Also, the slightly lower reactivity of the tetraacyloxysilanes is very valuable in the acylation of heterocyclic compounds of clearly aromatic nature; the acylation of selenophene with the tetraacyloxysilanes derived from monobasic acids and the monoethyl esters of dibasic acids is the most convenient method for the preparation of ketones and keto-acids of the selenophene series. Nesmeyanov, Perevalova, and coworkers[132], using tetraacetoxysilane to acetylate ferrocene, obtained the monoacetyl derivative, while acetyl chloride gave the diacetyl derivative of ferrocene.

Yur'ev and Belyakova have shown that tetraacyloxysilanes can successfully replace acid anhydrides in the acylation of compounds with a labile hydrogen atom, such as malonic and acetoacetic esters. The acylation of malonic ester[54,133,134] in the presence of magnesium oxide and copper acetate at 165°–170° produces symmetrical β-diketones of the type $RCOCH_2COR$, in yields of 34–37%:

$$CH_2(COOC_2H_5)_2+Si(OCOR)_4 \xrightarrow{-Si(OH)_4} 2(RCO)_2C(COOC_2H_5)_2 \xrightarrow[-C_2H_5OH,\ -CO_2]{+H_2O} 2RCOCH_2COR,$$

where R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, iso-C_4H_9, and n-C_5H_{11}.

The acylation of acetoacetic ester under the same conditions and with subsequent ketonic dissociation produces unsymmetrical β-diketones of the type CH_3COCH_2COR in yields of 34.5–77%[54,133,134]:

$$4CH_3COCH_2COOC_2H_5+Si(OCOR)_4 \xrightarrow[-C_2H_5OH\ -CO_2]{+H_2O} 4CH_3COCH_2COR,$$

where R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, and iso-C_4H_9.

The ability of tetraacyloxysilanes derived from saturated monobasic acids to acylate acetylene in the presence of aluminium chloride[135] is of great interest. The reaction apparently passes through an intermediate stage in which there is addition to the triple bond to form an ester of orthosilicic acid and a β-hydroxyvinyl alkyl ketone, which then dissociates to give a β-chlorovinyl alkyl ketone:

$$Si(OCOR)_4+CH{\equiv}CH \xrightarrow{AlCl_3} [Si(OCH{=}CHCOR)_4] \xrightarrow{AlCl_3} 4RCOCH{=}CHCl+Si(OAlCl_2)_4,$$

where R = CH_3, C_2H_5, n-C_3H_7, and n-C_5H_{11}.

An important property of tetraacyloxysilanes is the lability of the hydrogen atoms in the α-methylene group. Khaskin[136] studied the possible replacement of the hydrogen atoms in tetraacetoxysilane by deuterium, and found that in the presence of sodium acetate this exchange takes place to the extent of 92% in 25 h:

$$Si(OCOCH_3)_4+4CH_3COOD \longrightarrow Si(OCOCH_2D)_4+4CH_3COOH.$$

Because of the lability of the hydrogen atoms in the α-methylene groups, the condensation of tetraacetoxysilane with benzaldehyde by the Perkin reaction in the presence of sodium acetate takes place (although more slowly than the isotope exchange) even at 100°, which is too low a temperature for the condensation of benzaldehyde with lead acetate and acetic anhydride[114,136].

The condensation of tetraacyloxysilanes with aromatic aldehydes, furfural, and thiophene-2-aldehyde in the presence of salts of the corresponding acid or of potassium carbonate was studied in detail by Yur'ev, Elyakov, and Vysokosov, who obtained cinnamic acid (74.5% yield)[137], its homologues (22–69.5%)[138] and derivatives (36–89.5%)[139], and also furyl-2-acrylic acid and its homologues (26–70.5%) and thienyl-2-acrylic acid (80%)[140]:

$$2RCHO+Si(OCOCH_2R')_4 \xrightarrow{-Si(OH)_4} 2RCH{=}\underset{\displaystyle R'}{\overset{\displaystyle |}{C}}{-}COOH+2R'CH_2COOH.$$

The reaction of tetraacyloxysilanes with organomagnesium compounds had not been studied until recently; only in 1953–54 did Lanning describe the reactions between tetrapropionyloxysilane and ethylmagnesium bromide[39], and tetrabenzoyloxysilane and phenylmagnesium bromide[40]. According to his results, the products are triethylcarbinol and triphenylcarbinol respectively, and an unidentified silicon-containing compound. Lanning and Moore[41] reported in 1958 that they had isolated tertiary alcohols (in 56–59% yield) and an ethylsiloxane fraction of general formula $[(C_2H_5)_2SiO]_x$, where x = 3 or 4, from the reaction product of tetraacyloxysilanes with ethylmagnesium bromide. If the reaction is carried out with 80% of the required quantity of Grignard reagent, ketones (26–29%) can also be isolated, in addition to the tertiary alcohols (42–45%).

Yur'ev and Belyakova showed that the main products of the reaction between tetraacetoxysilane and alkylmagnesium halides (on longer boiling of the reaction mixture) are

tertiary alcohols (58–68.5% yields) and tetraalkylsilanes (51–72%), with higher-boiling fractions which are apparently siloxanes[141]:

$$Si(OCOCH_3)_4 + 12RMgX \longrightarrow 4CH_3R_2COH + SiR_4,$$

where R = CH_3, C_2H_5, n-C_3H_7, and n-C_5H_{11}.

The reaction of tetraacetoxysilanes with organocadmium compounds produces ketones in 20–46% yields[141]. The reaction is apparently as follows:

$$Si(OCOCH_3)_4 + 4RCdX \longrightarrow 4RCOCH_3 + Si(OCdX)_4.$$

2. Reactions of Acyloxytrichlorosilanes

Acyloxytrichlorosilanes are colourless, mobile, very hygroscopic liquids which fume strongly in air. They disproportionate ("symmetrise") relatively easily into silicon tetrachloride and tetraacyloxysilanes:

$$4RCOOSiCl_3 \longrightarrow 3SiCl_4 + Si(OCOR)_4.$$

Those derived from *o*-chloro- and *o*-nitrobenzoic acids are completely disproportionated in 1 h, and those derived from *p*-toluic and benzoic acids in a month. All acyloxytrichlorosilanes disproportionate when distilled, some partially, others completely. The tendency of the fatty acid derivatives to disproportionate decreases with increase in the length of the carbon chain and with increase in the degree of branching in the chain. This tendency increases with increasing strength of the acid. Disproportionation is also favoured by reduced pressure, increased temperature, and small amounts of the starting acid[53,54,56].

Acyloxytrichlorosilanes are active acylating agents for aromatic compounds (benzene, thiophene)[142]. The yields of ketones when benzene is acylated are considerably higher than when acylating with tetraacyloxysilanes. For instance, the yields of substituted benzophenones (70–88%) are as good as those obtained in the acylation of benzene with substituted benzoyl chlorides.

The yields of the corresponding ketones in the acylation of thiophene with acyloxytrichlorosilanes in the presence of stannic chloride, as when tetraacyloxysilanes are used, are 60–95%[55,142].

The acyloxy group in the acyloxytrichlorosilanes is highly reactive; the action of 1 mole of anhydrous ethyl alcohol at -30° substitutes an ethoxy group for the acyloxy group more easily than for the chlorine atom, and the acid is obtained in 66–72% yield, possibly as a result of the catalytic influence of the hydrogen chloride liberated in the partial replacement of the chlorine atom by the alkoxy group. The reaction of acyloxytrichlorosilanes with acids produces mixed anhydrides of silicic acid and the two different organic acids[55,56]:

$$RCOOSiCl_3 + 3R'COOH \longrightarrow RCOOSi(OCOR')_3 + 3HCl.$$

With organomagnesium compounds, acyloxytrichlorosilanes behave similarly to tetraacyloxysilanes, forming tertiary alcohols (74–89% yields) and tetraalkylsilanes (53–72% yields)[55,56].

3. Reactions of Alkyl-, Alkylalkoxy-, and Alkoxyacyloxysilanes

Alkylacyloxysilanes are solids or liquids with a pleasant ethereal smell[73], unstable to heating. Thus methylphenyldiacetoxysilane decomposes on heating to 200° into acetic anhydride and polymethylphenylsiloxane[82]:

$$xCH_3(C_6H_5)Si(OCOCH_3)_2 \longrightarrow x(CH_3CO)_2O + [CH_3(C_6H_5)SiO]_x.$$

Triphenylacetoxysilane decomposes on distillation in a vacuum (3 mm Hg)[75], but triphenylformyloxysilane is stable to heating to 180°[60]. Characteristic of unsymmetrical alkylacyloxy- and alkoxyacyloxysilanes, as with all organosilicon compounds, is their ability to disproportionate on heating to form symmetrical molecules[101], e.g.:

$$2CH_3COOSi(OC_2H_5)_3 \longrightarrow (CH_3COO)_2Si(OC_2H_5)_2 + Si(OC_2H_5)_4.$$

Alkylacyloxysilanes are hydrolysed with varying degrees of ease; the most easily hydrolysed are alkyltriacetoxysilanes[7,80,82]; dialkyldiacyloxysilanes are hydrolysed almost as easily[7,79,88]. The hydrolysis products are mainly polysiloxanes.

Trialkylacyloxysilanes are hydrolysed by water with considerably more difficulty[58,90,98], with the exception of those prepared from dibasic acids[58].

According to Larsson's results, alkylalkoxyacyloxysilanes are hydrolysed much more rapidly in a homogeneous medium, and in the presence of ammonia, sodium carbonate, and caustic potash[143].

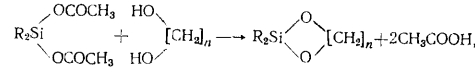
Andrianov and coworkers and Dolgov and coworkers showed that when alkylacetoxysilanes react with alcohols, an alkoxy group replaces the acetoxy group, with the liberation of acetic acid[69,72,81,109]:

$$R_xSi(OCOCH_3)_{4-x} + yR'OH \longrightarrow R_xSi(OCOCH_3)_{4-x-y}(OR')_y + yCH_3COOH.$$

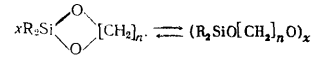
Tertiary alcohols react with more difficulty than primary and secondary alcohols[69].

Andrianov and Dubrovina studied the reaction of alkylacetoxysilanes with glycidol and showed that as the number of acetoxy groups in the silane decreases, it becomes more difficult to replace them by glycidol residues, and, for example, trimethylacetoxysilane does not undergo substitution in this way[72].

Davydova, Voronkov, and Dolgov established that the reaction between dialkyldiacetoxysilanes and β-, γ-, δ-, and ε-glycols produces cyclic ethers of dialkylsilanediols containing 6-, 7-, 8-, and 9-membered rings in 50–70% yields:



where n = 3–6. The reaction is accomplished by mixing the reagents and distilling off the resulting acetic acid in a vacuum. If the acid is distilled at atmospheric pressure, the main reaction product is the glycol acetate. The residue after the vacuum distillation is a polymer, and only after thermal depolymerisation (by sublimation in a vacuum), accompanied by rearrangement of the Si–O–C bonds, is the expected cyclic ether formed. The depolymerisation is reversible, and on standing the cyclic ethers again polymerise:



Attempts to obtain five-membered cyclic ethers by reacting dimethyldiacetoxysilane with ethylene and propylene glycols produced in both cases dimers containing the 1,3,6,8-tetraoxa-2,7-disilacyclodecane ring[116,144].

Davydova, Voronkov, and Dolgov also established that dialkyldiacetoxysilanes react smoothly with pentaerythritol to form spirocyclic ethers of dialkylsilanediols:

$$2R_2Si(OCOCH_3)_2+(HOCH_2)_2C(CH_2OH)_2 \longrightarrow$$

$$\longrightarrow R_2Si\begin{matrix}O-CH_2\\O-CH_2\end{matrix}C\begin{matrix}CH_2-O\\CH_2-O\end{matrix}SiR_2+4CH_3COOH.$$

The reaction of dialkyldiacetoxysilanes with glycerol did not produce derivatives of the type

$$R_2Si\begin{matrix}O-CH_2\\O-CH_2\end{matrix}CHOH;$$

with R = C_2H_5, a compound was obtained of formula $C_{18}H_{40}O_6Si_3$; with R = CH_3, the product had the composition $C_7H_{18}O_5Si$, and contained two hydroxy groups and one acetoxy group; one of the hydroxy groups was attached to the silicon atom[116,145].

As mentioned above, the reaction of alkylacyloxysilanes with acids[76,77,100] is the basis of Anderson's method for the synthesis of alkylacyloxysilanes derived from acids of low volatility. Anderson[75] and Andrianov and coworkers[146] showed that with acid chlorides and with phosphorus tribromide[75], alkylacyloxysilanes give alkylhalogenosilanes:

$$R_xSi(OCOR')_{4-x}+(4-x)R''COCl \longrightarrow R_xSiCl_{4-x}+(4-x)R'COOCOR'',$$

$$3(CH_3)_3SiOCOCH_2Cl+PBr_3 \longrightarrow 3(CH_3)_3SiBr+P(OCOCH_2Cl)_3.$$

Only one instance of the reaction of alkylacyloxysilanes with a Grignard reagent has been studied. Methyldibutylcarbinol was prepared by the action of trimethylacetoxysilane on butylmagnesium bromide; no silicon-containing product was isolated[61].

Henglein and Schmulder[97] and Andrianov and coworkers[146] showed that diacyloxysilanes react with di- and trialkoxysilanes[97,146], phenyltrichlorosilane[146], and esters of boric acid[147] to form poly-organosiloxanes and poly-organoborosiloxanes respectively.

In his study of the exchange reactions of alkylacyloxysilanes with silver oxide and salts Anderson established that the acyloxysilanes do not react with silver iodide, chloride, bromide, sulphide, isocyanate, or isothiocyanate, react to a slight extent with silver cyanide, and better with silver fluoride, silver oxide, and the silver salts of organic acids[77].

Heating alkylacyloxysilanes with zinc and aluminium chlorides produces the corresponding alkylchlorosilanes[148,149].

According to Bradley and Thomas[150], the reaction of trialkylacetoxysilanes with alkoxy derivatives of titanium, zirconium, and tantalum can be used to prepare the trialkylsiloxy derivatives of these metals:

$$nR_3SiOCOCH_3+M(OR')_n \longrightarrow nR'OCOCH_3+M(OSiR_3)_n.$$

However, Andrianov and Ganina[151] showed that trimethylacetoxysilane and titanium tetrabutoxide do not react in this way, but produce a mixture of octaacetoxycyclotetratitanoxane, $[TiO(OCOCH_3)_2]_4$, and heptaacetoxytrimethylsiloxycyclotetratitanoxane, $[(CH_3COO)_2TiO]_3OTi(OCOCH_3)\cdot OSi(CH_3)_3$.

The main reaction is therefore replacement of butoxy groups by acetoxy groups. The reaction between trimethylacetoxysilane and titanium tetrachloride similarly takes place with exchange of chlorine for acetoxy groups, with the formation of cyclic polymers. The formation of compounds containing the Si–O–Ti group takes place with difficulty.

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Faculty of Chemistry,
Lomonosov Moscow State University

POLYMERISATION OF ISOBUTENE

Ya. T. Eidus and B. K. Nefedov

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INTRODUCTION

As is well known, much attention is now being paid to development of the chemical industry in this country, and in particular to production of high polymers, plastics, synthetic rubbers, and fibres. Products from the processing of gas and petroleum must form the basic raw materials for this new growth of the chemical industry.

In recent years processes for polymerising and copolymerising unsaturated compounds, particularly alkenes (ethylene, its homologues, and derivatives), have become important. The study of alkene polymerisation is based on the work of Russian and Soviet chemists, in the first place that of A. M. Butlerov. Both in the USSR and elsewhere the industrial utilisation of alkene-polymerisation processes for industrial gases has been under investigation for some decades; useful catalysts have been sought and prepared, and reaction mechanisms studied. It has been found that various acids (sulphuric, phosphoric, and hydrofluoric), natural and artificial aluminosilicates, halides of certain elements (aluminium, boron, zinc, titanium, tin, etc.), and individual metal oxides, are catalysts for polymerising the simplest alkenes to produce liquid products (motor spirits and viscous oils). More recently the polymerisation of alkenes to macromolecular solid polymers (polythene, polypropylene) has acquired great theoretical and practical interest. This can take place at ultra-high pressures in the presence of initiators (oxygen, organic peroxides), and also at atmospheric or elevated pressures in the presence of catalysts (metal oxides, organic aluminium compounds and titanium tetrachloride).

Of the alkene monomers used in industrial polymerisation processes, special interest attaches to isobutene, ethylene, and propene. Isobutene is a relatively accessible substance, which polymerises to a number of valuable products, superior in some respects to similar products obtained from other alkenes. Among these may be mentioned the isomeric isooctenes which are hydrogenated to isooctane (valuable as a petrol additive), high-quality lubricating oils, synthetic rubbers, and plastics.

The present article is a review of literature and patent information on isobutene polymerisation. Catalytic polymerisation of isobutene is of great practical importance and particular attention is given to it.

I. POLYMERISATION OF ISOBUTENE BY HEAT, FREE RADICALS, AND OTHER ACTIVE PARTICLES

1. Action of Heat

It has been shown that isobutene[1] and t-butanol[2] decompose at dark-red heat, giving complex mixtures of products. According to Ipat'ev[3] polymerisation of isobutene in an iron tube at 380°–390°, with an initial pressure of 70 atm, leads to formation of a mixture of liquid saturated, unsaturated, and naphthenic hydrocarbons.